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11

Publication number:

0 308 179 B1

12

EUROPEAN PATENT SPECIFICATION

- 45 Date of publication of patent specification: 27.04.94
- 51 Int. Cl.5: C08L 23/02, C08L 53/00, C08L 69/00, //(C08L23/02,53:00, 69:00),(C08L53/00,23:02,69:00), (C08L69/00,53:00,23:02)
- 21 Application number: 88308458.4
- 22 Date of filing: 13.09.88

54 Thermoplastic resin composition.

- 30 Priority: 17.09.87 JP 234277/87
17.09.87 JP 234278/87
17.09.87 JP 234279/87
17.09.87 JP 234280/87
17.09.87 JP 234281/87
17.09.87 JP 234282/87
17.09.87 JP 234283/87
17.09.87 JP 234284/87
17.09.87 JP 234285/87

43 Date of publication of application:
22.03.89 Bulletin 89/12

45 Publication of the grant of the patent:
27.04.94 Bulletin 94/17

84 Designated Contracting States:
DE FR GB

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Description

The present invention relates to a thermoplastic resin composition with good mechanical strength, impact resistance, thermal deformation resistance, moldability and chemical resistance comprising crystalline polyolefin, polycarbonate and additive components.

Aromatic polycarbonates have excellent impact strength, heat resistance, rigidity and dimension stability, but they are poor in solvent resistance and moldability. To overcome these problems, attempts have been made to provide polycarbonate compositions with polyolefins. However, since polyolefins and polycarbonates do not have good compatibility, proposals have been made to add various third components to improve their compatibility.

Japanese Patent Laid-Open No. 57-108151 discloses a polycarbonate resin composition comprising 100 parts by weight of a polycarbonate resin, 0.3-20 parts by weight of polyethylene and 0.3-20 parts by weight of a butyl rubber.

Japanese Patent Laid-Open No. 57-108152 discloses a polycarbonate resin composition comprising 0.3-20 parts by weight of an ethylene-propylene copolymer and/or an ethylene-propylene-diene copolymer as a third component.

Japanese Patent Laid-Open No. 57-111351 discloses a polycarbonate resin composition comprising 0.3-20 parts by weight of an isoprene rubber and/or a methylpentene polymer as a third component.

Any of these polycarbonate resin compositions, however, suffers from drastic decrease in impact strength when polyethylene content exceeds 10 %, resulting in the surface peel of molded products.

Further, there are various proposals in adding third components. For instance, Japanese Patent Laid-Open Nos. 56-76449 and 59-133247 disclose thermoplastic resin compositions comprising polycarbonate, polyolefin and an ABS resin. However, the ABS resin do not have sufficient effects of increasing compatibility, so when polyolefin exceeds 10 %, the thermoplastic resin compositions lose mechanical strength.

Japanese Patent Laid-Open No. 59-196360 discloses a polycarbonate resin composition comprising as a third component a copolymer of at least one olefin and an acrylate, methacrylate, acrylic acid or methacrylic acid monomer, for instance, an ethylene-ethyl acrylate copolymer (EEA resin).

Japanese Patent Laid-Open No. 61-215649 discloses a polycarbonate resin composition comprising as a third component an olefin-vinyl ester copolymer, for instance, an ethylene-vinyl acetate copolymer (EVA resin), etc.

However, these compositions also suffer from decrease in impact strength due to the decrease in compatibility when the amount of polyolefin nears that of polycarbonate.

Japanese Patent Laid-Open No. 61-115945 discloses a composition comprising a styrene-ethylene-butylene-styrene block copolymer (SEBS resin) as a third component. However, the addition of the SEBS resin fails to provide sufficient rigidity, thermal deformation resistance, impact strength, and surface peel resistance, though the compatibility is slightly improved.

Japanese Patent Publication Nos. 51-24540 and 51-41145 and Japanese Patent Laid-Open No. 60-233151 disclose thermoplastic resin compositions comprising polycarbonate and a graft copolymer produced by grafting a styrene monomer and acrylonitrile monomer to an ethylene-propylene-diene copolymer (AES resin). However, since none of these thermoplastic resin compositions contains polyolefin, they are poor in moldability.

In addition, Japanese Patent Laid-Open Nos. 61-159447, 61-120852, 61-225245, 61-235456 and 61-238847 disclose compositions comprising aromatic polycarbonate, polyester and/or modified polyolefin, etc.

Further, Japanese Patent Laid-Open No. 49-76948 discloses a thermoplastic resin composition comprising polycarbonate and a styrene-maleic anhydride copolymer. However, since no polyolefin is contained in these compositions, they are poor in solvent resistance.

EP-A-0230609 discloses a resin composition comprising a blend of a polycarbonate resin and a graft copolymer together with at least one of a polyolefin, an olefin acrylate or methacrylate copolymer or a copolymer of a vinyl aromatic compound and an olefin elastomer.

Journal of Elastomers and Plastics, vol. 14, 1982 pp148-154 discloses a thermoplastic resin composition comprising polypropylene, polycarbonate and styrene-ethylene-butylene-styrene block copolymer. This composition has poor surface peel resistance and poor Izod impact strength.

As described above, although thermoplastic resin compositions based on polycarbonate and polyolefin whose compatibility is improved to have an excellent balance of mechanical strength, moldability and solvent resistance are desired particularly for automobile parts, satisfactory compositions have never been provided.

OBJECT AND SUMMARY OF THE INVENTION

An object of the present invention is, therefore, to increase the compatibility between polycarbonate and polyolefin, thereby not only improving impact strength, thermal deformation resistance, moldability and chemical resistance but also preventing surface peel.

Another object of the present invention is to provide a polycarbonate resin composition having a well-balanced combination of mechanical strength, moldability, and solvent resistance, with improved compatibility between polycarbonate and polyolefin.

As a result of intense research in view of the above objects, it has been found that particular additive components as described below can drastically improve the compatibility between polycarbonate and polyolefin, thereby providing thermoplastic resin compositions with excellent mechanical strength, impact resistance, thermal deformation resistance, moldability, and solvent resistance. The present invention has been completed based on this finding.

The thermoplastic resin composition according to a first embodiment of the present invention comprises (a) 95-5 weight % of crystalline polyolefin having a crystallinity of 20 % or more, (b) 5-95 weight % of polycarbonate, and (c) 5-100 parts by weight, per 100 parts by weight of said (a) + said (b), of a styrene-ethylene-propylene block copolymer having a weight average molecular weight of 10 000 - 1 000 000 and a weight ratio of styrene to ethylene = propylene of 15/85 - 70/30.

The thermoplastic resin composition according to a second embodiment of the present invention comprises (a) 95-5 weight % of crystalline polyolefin having a crystallinity of 20% or more, (b) 5-95 weight % of polycarbonate, (c) a styrene-ethylene-butylene-styrene block copolymer having a weight average molecular weight of 10 000 - 1 000 000 and a weight ratio of styrene to ethylene-butylene of 10/90 - 70/30, and (d) a low-crystallinity ethylene- α -olefin copolymer having a weight average molecular weight of 30 000 - 1 000 000 and a crystallinity of less than 20% and a weight ratio of, ethylene to α -olefin of 20/80 - 85/15 said (c) + said (d) being 5-100 parts by weight per 100 parts by weight of said (a) + said (b), and a weight ratio of said (c) to said (d) being 30/70- 95/5.

DETAILED DESCRIPTION OF THE INVENTION

Polycarbonates, particularly aromatic polycarbonates which can be used in the present invention may be produced by (a) a reaction between bivalent phenol and a carbonate precursor such as phosgene in the presence of an acid acceptor and a molecular weight modifier, or (b) a transesterification reaction between bivalent phenol and a carbonate precursor such as diphenyl carbonate. The bivalent phenols which can be used are preferably bisphenols, particularly 2,2-bis (4-hydroxyphenyl) propane (bisphenol A). Part or total of bisphenol A may be replaced by other bivalent phenols. The other bivalent phenols than bisphenol A include hydroquinone, 4,4'-dihydroxydiphenyl, bis (4-hydroxyphenyl) alkane, bis (4-hydroxyphenyl) cycloalkane, bis (4-hydroxyphenyl) sulfide, bis (4-hydroxyphenyl) sulfone, bis (4-hydroxyphenyl) sulfoxide, bis (4-hydroxyphenyl) ketone, and bis (4-hydroxyphenyl) ether, and halogenated bisphenols such as bis (3,5-dibromo-4-hydroxyphenyl) propane. Homopolymers or copolymers of these bivalent phenols or their mixtures may also be used. Such polycarbonate resins are commercially available.

The aromatic polycarbonate preferably has a weight-average molecular weight of 10,000-100,000. When it is less than 10,000, sufficient mechanical properties cannot be provided, and when it exceeds 100,000, the moldability decreases. The more preferable weight-average molecular weight is 20,000-50,000.

Crystalline polyolefins which can be used in the present invention include polyethylene, polypropylene, polybutene-1, poly-4-methylpentene-1 and other α -olefin polymers, and the preferred polyolefin is polypropylene. Incidentally, the polyolefin need not be a homopolymer. For instance, in the case of polypropylene, it may be a copolymer of propylene with up to 20 weight % of other one or more α -olefins. The preferred comonomers for the propylene copolymer include ethylene. The copolymers may be random copolymers, block copolymers or graft copolymers. The weight-average molecular weight of the polyolefin is 10,000-1,000,000, and preferably 30,000-300,000. Further, it has a melt flow rate (MFR) of 500-0.01 g/10 min at 230 °C, and preferably 50-1 g/10 min.

When measured by an X-ray diffraction method, the polyolefin has a crystallinity of 20% or more. When the crystallinity is less than 20%, the resulting thermoplastic resin composition has low mechanical strength. The preferred crystallinity is 40 % or more.

In the present invention, a weight ratio of the crystalline polyolefin to the polycarbonate is 95-5% to 5-95%. When the polycarbonate is less than 5 weight %, sufficient impact strength and mechanical strength cannot be obtained, and when it exceeds 95 weight %, the moldability and the solvent resistance decrease. Preferably, the polyolefin is 90-10 weight %, and the polycarbonate is 10-90 weight %. More preferably, the

polyolefin is 80-20 weight %, and the polycarbonate is 20-80 weight %.

In the first embodiment of the present invention, the styrene-ethylene-propylene block copolymer is a block copolymer composed of a styrene moiety and an ethylene-propylene moiety both in the form of blocks. A styrene/ethylene-propylene weight ratio in the styrene-ethylene-propylene block copolymer is 15/85 - 70/30. When it is less than 15/85, sufficient mechanical strength cannot be obtained, and when it exceeds 70/30, the resulting thermoplastic resin composition becomes brittle. The preferred styrene/ethylene-propylene weight ratio is 20/80 - 50/50. Further, the styrene-ethylene-propylene block copolymer has a weight-average molecular weight of 10,000-1,000,000. When it is less than 10,000, sufficient mechanical strength cannot be obtained, and when it exceeds 1,000,000, good dispersion of the styrene-ethylene-propylene block copolymer in the composition cannot be achieved.

The styrene-ethylene-propylene block copolymer can be prepared by first producing a styrene-isoprene block copolymer and then hydrogenating unsaturated bonds of isoprene. The styrene-isoprene block copolymer can be prepared by a usual anion living polymerization method, and its hydrogenation can be conducted by using a hydrogenation catalyst such as a nickel catalyst carried on a diatomaceous earth. However, it should be noted that styrene-ethylene-propylene block copolymers produced by any other methods can be used in the present invention.

The amount of the styrene-ethylene-propylene block copolymer added is 5-100 parts by weight per 100 parts by weight of the crystalline polyolefin + the polycarbonate. When it is less than 5 parts by weight, the resulting thermoplastic resin composition has insufficient impact resistance, surface peel resistance and mechanical strength, and when it exceeds 100 parts by weight, the rigidity of the composition decreases dramatically, making the composition unusable in practical applications. The preferred amount of the styrene-ethylene-propylene block copolymer is 10-50 parts by weight, and the more preferable amount is 15-40 parts by weight.

The thermoplastic resin composition according to the second embodiment of the present invention is characterized by comprising the styrene-ethylene-butylene-styrene block copolymer and the low-crystallinity ethylene- α -olefin copolymer as third and fourth components.

The styrene-ethylene-butylene-styrene block copolymer is a block copolymer composed of a styrene moiety and an ethylene-butylene moiety both in the form of blocks. A weight ratio of styrene/ethylene-butylene in the styrene-ethylene-butylene-styrene block copolymer is 10/90 - 70/30. When it is less than 10/90, sufficient mechanical strength cannot be obtained, and when it exceeds 70/30, the resulting thermoplastic resin composition becomes brittle. The preferred styrene/ethylene-butylene weight ratio is 20/80 - 50/50. Further, the styrene-ethylene-butylene-styrene block copolymer has a weight-average molecular weight of 10,000-1,000,000. When it is less than 10,000, sufficient mechanical strength cannot be obtained, and when it exceeds 1,000,000, good dispersion of the styrene-ethylene-butylene-styrene block copolymer in the composition cannot be achieved. Incidentally, the styrene moiety is not limited to that composed only of styrene, but may be made of substituted styrene such as methylstyrene.

The styrene-ethylene-butylene-styrene block copolymer can be produced by methods disclosed in U.S. Patents 3,595,942 and 4,188,432. Specifically, a styrene-butadiene-styrene block copolymer is treated at a temperature of 25-175 °C in the presence of a catalyst composed of a cobalt or nickel alkoxide reduced by an alkyl aluminum compound to selectively hydrogenate the butadiene moiety, thereby converting it to a structure corresponding to an ethylene-butene-1 copolymer. Incidentally, the styrene-ethylene-butylene-styrene block copolymer produced any other methods can be used in the present invention.

The low-crystallinity ethylene- α -olefin copolymer is a copolymer of ethylene and α -olefins such as propylene, butylene, and pentene, and particularly preferable low-crystallinity ethylene- α -olefin copolymers are an ethylene-propylene rubber and an ethylene-butylene rubber. A weight ratio of ethylene to α -olefin is 20:80-85:15. When it is less than 20:80 or when it exceeds 85:15, the elasticity is decreased. The preferred ethylene/ α -olefin weight ratio is 30:70-70:30. Incidentally, it should be noted that the low-crystallinity ethylene- α -olefin copolymer may contain two or more types of α -olefins.

The low-crystallinity ethylene- α -olefin copolymer has a weight-average molecular weight of 30,000-1,000,000. When it is less than 30,000, the resulting composition does not have sufficient strength, and when it exceeds 1,000,000, good dispersion of the low-crystallinity ethylene- α -olefin copolymer cannot be achieved. The preferred weight-average molecular weight is 50,000-200,000. Further, it has a crystallinity of 20% or less when measured by an X-ray diffraction method. The preferred crystallinity is 0-10%. In addition, it has a melt flow rate (MFR) of 0.01-50 g/10 min at 230 °C, and preferably 0.1-20 g/10 min.

A total amount of the styrene-ethylene-butylene-styrene block copolymer and the low-crystallinity ethylene- α -olefin copolymer is 5-100 parts by weight per 100 parts by weight of the crystalline polyolefin + the polycarbonate. When it is less than 5 parts by weight, the resulting thermoplastic resin composition does not have sufficient impact resistance, surface peel resistance and mechanical strength, and when it

exceeds 100 parts by weight, the rigidity of the composition decreases dramatically, making it unusable in practical applications. Preferably, the total amount is 10-50 parts by weight, and more preferably, it is 20-40 parts by weight.

A weight-ratio of the styrene-ethylene-butylene-styrene block copolymer to the low-crystallinity ethylene- α -olefin copolymer is 30:70-95:5. When it is less than 30:70, sufficient compatibility cannot be provided between the polyolefin and the polycarbonate, and when it exceeds 95:5, the surface peel resistance and the impact strength are lowered. The preferred weight ratio is 50:50-90:10.

The present invention will be explained in further detail referring to the following Examples.

The measurement of the properties of the thermoplastic resin compositions were conducted in each
 10 Example and Comparative Example as follows:

(1) Flexural modulus

Measured according to ASTM D790.

(2) Izod impact strength

Measured according to ASTM D256 at 23 °C and -30 °C, respectively.

15 (3) Dynamic melt viscosity

Measured by a dynamic spectrometer of Rheometrix at 250 °C and 100 rad/sec.

(4) Surface peel resistance

The surface of each sample was cut by a razor in a checkered pattern to have 100 checkers of 1 mm x 1 mm. An adhesive cellophane tape (manufactured by Nichiban Co., Ltd.) was adhered onto the sample
 20 surface and then peeled off. The number of remaining checkers was counted.

(5) Weight change by methanol immersion

Each sample was immersed in methanol at 25 °C for 30 days and the change in its weight was measured.

(6) Tensile elongation at break

25 Measured according to ASTM D 638.

(7) Heat deflection temperature

Measured according to ASTM D648 and shown by a temperature at which a test piece (cantilever) was distorted by a predetermined amount (0.254 mm) under a constant load (4.6 kg/cm²) when the temperature was elevated at a constant rate of 2 °C/min.

30 (8) Thermal deformation temperature

Measured according to JIS K7207, and shown by a temperature at which a test piece (cantilever) was deformed by a predetermined amount (0.25 mm) under a constant load (4.6 kg/cm²) when the temperature was elevated at a constant rate of 2 °C/min.

35 Example 1

Crystalline polypropylene (MFR = 9.0 g/10 min), a polycarbonate resin (Panlite™ L 1225 manufactured by Teijin Chemicals, Ltd.) and a styrene-ethylene-propylene block copolymer (Kraton G™ 1701 manufactured by Shell Kagaku K.K., a styrene/rubber weight ratio = 37/63) were mixed in the proportions shown in
 40 Table 1 at room temperature in a Henschel mixer. The resulting mixture was kneaded at 250 °C in a double-screw extruder to provide composition pellets.

The resulting thermoplastic resin composition was measured with respect to flexural modulus, Izod impact strength, dynamic melt viscosity, surface peel resistance and solvent resistance (weight change by methanol immersion). The results are shown in Table 1.

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Examples 2-5 and 8

Example 1 was repeated except for changing the proportions of the crystalline polypropylene, the polycarbonate and the styrene-ethylene-propylene block copolymer as shown in Table 1, and the prop-
 50 erties of the resulting thermoplastic resin compositions were measured. The results are shown in Table 1.

Example 6

Example 2 was repeated except for replacing 10 parts by weight of the polypropylene by an ethylene-propylene rubber (Tafmer P™ 0180 manufactured by Mitsui Petrochemical Industries, Ltd.), and the
 55 roperties of the resulting thermoplastic resin composition were measured. The results are shown in Table 1.

Example 7

Example 2 was repeated except for using as the crystalline polypropylene a propylene block copolymer (BJ 309 manufactured by Tonen Sekiyu Kagaku K.K., propylene = 92.7 weight %, ethylene 7.3 weight %, MFR = 9 g/10 min), and the properties of the resulting thermoplastic resin composition were measured. The results are shown in Table 1.

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Table 1

| Example No. | Composition (Weight %) | | SEP (3) | Flexural Modulus X 10 ⁴ Pa ₂ (kgf/cm ²) | Properties | | | |
|-------------|------------------------|--------|---------|---|--|--|-------------------------|------------------------|
| | PP (1) | PC (2) | | | Izod Impact Strength X 10 ² Pa (kgf/cm ²) at 23°C | Dynamic Viscosity (x10 ³ poise) | Surface Peel Resistance | Solvent Resistance (4) |
| 1 | 70 | 20 | 10 | 112776 (11500) | 89.3 (8.9) | 240 (2.4) | 100 | 0.27 |
| 2 | 50 | 30 | 20 | 82337 (8600) | 205.4 (21.0) | 280 (2.8) | 100 | 0.36 |
| 3 | 40 | 40 | 20 | 90221 (9200) | 351.0 (35.8) | 310 (3.1) | 100 | 0.38 |
| 4 | 30 | 50 | 20 | 93163 (9500) | 454.0 (46.3) | 340 (3.4) | 100 | 0.46 |
| 5 | 20 | 70 | 10 | 154945 (15800) | 584.5 (59.6) | 700 (7.0) | 100 | 0.74 |
| 6 | 40 | 30 | 20 | 75511 (7700) | 206.9 (21.1) | 250 (2.5) | 100 | 0.37 |
| 7 | 50 (6) | 30 | 20 | 77472 (7900) | 241.2 (24.6) | 270 (2.7) | 100 | 0.36 |
| 8 | 20 | 40 | 40 | 6685 (6800) | 475.6 (48.5) | 390 (3.9) | 100 | 0.40 |

Note: (1) Polypropylene

(2) Polycarbonate

(3) Styrene-ethylene-propylene block copolymer

(4) Weight change by methanol immersion (weight %)

(5) Ethylene-propylene rubber (TafmerTM 0180 manufactured by Mitsui Petrochemical Industries, Ltd.)

(6) Propylene 'block copolymer (BJ 309 manufactured by Tonen Sekiyu Kagaku K.K.,

MFR = 9 g/10 min)

55 Comparative Examples 1, 2

Thermoplastic resin compositions were prepared in the same manner as in Example 1 except for using a two-component system consisting of the crystalline polypropylene and the polycarbonate, and their

properties were measured. The results are shown in Table 2.

Comparative Example 3

5 Example 2 was repeated except for replacing the styrene-ethylene-propylene block copolymer by a styrene-ethylene-butylene-styrene block copolymer (Kraton G 1650 manufactured by Shell Kagaku K.K.), and the properties of the resulting thermoplastic resin composition were measured. The results are shown in Table 2.

10 Comparative Example 4

Example 2 was repeated except for replacing the styrene-ethylene-propylene block copolymer by an ethylene-vinyl acetate copolymer (NUC DQ DJ 3269 manufactured by Nippon Unicar Co., Ltd.), and the properties of the resulting thermoplastic resin composition were measured. The results are shown in Table 2.

Comparative Example 5

20 Example 2 was repeated except for replacing the styrene-ethylene-propylene block copolymer by an ethylene-ethyl acrylate copolymer (NUC 6570 manufactured by Nippon Unicar Co., Ltd.), and the properties of the resulting thermoplastic resin composition were measured. The results are shown in Table 2.

Comparative Example 6

25 In the case of 100 weight % polycarbonate, the resin's properties were similarly measured. The results are shown in Table 2.

Comparative Example 7

30 A thermoplastic resin composition was prepared in the same manner as in Example 2 except for reducing the amount of the styrene-ethylene-propylene block copolymer to 3 weight %, and its properties were measured. The results are shown in Table 2.

Comparative Example 8

35 A thermoplastic resin composition was prepared in the same manner as in Example 2 except for increasing the amount of the styrene-ethylene-propylene block copolymer to 60 weight % (150 parts by weight per 100 parts by weight of polypropylene + polycarbonate), and its properties were measured. The results are shown in Table 2.

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Table 2

| Comparative Example No. | Composition (Weight %) | | Flexural Modulus X 10 ⁴ Pa | Izod Impact Strength X 10 ⁴ Pa at 23°C | Izod Impact Strength X 10 ⁴ Pa at -30°C | Properties Dynamic Melt Viscosity Pa.s (x10 ³ poise) | Surface Peel Resistance | Solvent Resistance (4) |
|-------------------------|------------------------|--------|---------------------------------------|---|--|---|-------------------------|------------------------|
| | PP (1) | PC (2) | | | | | | |
| 1 | 70 | 30 | 151022 (15400) | 304 (3.1) | 35.3 (3.6) | 610 (6.1) | 0 | 0.27 |
| 2 | 50 | 50 | 155926 (15900) | 382 (3.9) | 40.2 (4.1) | 810 (8.1) | 0 | 0.48 |
| 3 | 50 | 30 | 9105 (9800) | 71.4 (8.0) | 33.3 (3.4) | 390 (3.9) | 85 | 0.37 |
| 4 | 50 | 30 | 10028 (10200) | 54.9 (5.8) | 26.5 (2.6) | 320 (3.2) | 0 | 0.38 |
| 5 | 50 | 30 | 8237 (8600) | 44.1 (4.5) | 22.6 (2.3) | 320 (3.2) | 60 | 0.40 |
| 6 | - | 100 | 191280 (19500) | 612.9 (62.5) | 122.6 (12.5) | 1600 (16) | 100 | 1.60 |
| 7 | 67 | 30 | 135332 (13800) | 51.0 (5.2) | 33.3 (3.4) | 240 (2.8) | 18 | 0.37 |
| 8 | 20 | 20 | 27459 (2800) | 627.6 (64.0) | 387.4 (39.5) | 560 (5.6) | 100 | 1.02 |

- Note: (1) Polypropylene
 (2) Polycarbonate
 (3) Styrene-ethylene-propylene block copolymer
 (4) Weight change by methanol immersion (weight %)
 (5) Styrene-ethylene-butylene-styrene block copolymer (Kraton G 1650 manufactured by Shell Kagaku K.K.)
 (6) Ethylene-vinyl acetate copolymer (NUC PQ DJ 3269 manufactured by Nippon Unicar Co., Ltd.)
 (7) Ethylene-ethyl acrylate copolymer (NUC 6570 manufactured by Nippon Unicar Co., Ltd.)

It is clear from Tables 1 and 2 that the thermoplastic resin compositions of the present invention have much better flexural modulus, impact strength, moldability (shown by dynamic melt viscosity), surface peel resistance and solvent resistance than those outside the scope of the present invention (Comparative Examples).

Examples 9-15

Crystalline polypropylene (MFR = 9.0 g/10 min), a polycarbonate resin (Panlite L™ 1225 manufactured by Teijin Chemicals, Ltd.), a styrene-ethylene-butylene-styrene block copolymer (Kraton G™ 1650 manufactured by Shell Kagaku K.K., a styrene/rubber weight ratio = 28/72) and an ethylene-propylene rubber (Tafmer™ P0180 manufactured by Mitsui Petrochemical Industries, Ltd.) were mixed in the proportions shown in Table 3 at room temperature in a Henschel mixer. Each of the resulting mixtures was then kneaded at 250 °C in a double-screw extruder to provide composition pellets.

The resulting thermoplastic resin compositions were measured with respect to flexural modulus, Izod impact strength, tensile elongation at break, dynamic melt viscosity, surface peel resistance and solvent resistance (weight change by methanol immersion). The results are shown in Table 3.

Example 16

Example 11 was repeated except for replacing the ethylene-propylene rubber by 10 parts by weight of an ethylene-butene-1 copolymer (Tafmer™ A 4085 manufactured by Mitsui Petrochemical Industries, Ltd.), and the properties of the resulting thermoplastic resin composition were measured. The results are shown in Table 3.

Example 17

Example 11 was repeated except for using as the crystalline polypropylene a propylene block copolymer (BJ 309 manufactured by Tonen Sekiyu Kagaku K.K., propylene = 92.7 weight %, ethylene = 7.3 weight %, MFR = 9 g/10 min), and the properties of the resulting thermoplastic resin composition were measured. The results are shown in Table 3.

Example 18

Example 11 was repeated except for using as the styrene-ethylene-butylene-styrene copolymer Kraton™ G 1657 (manufactured by Shell Kagaku K.K., a styrene/rubber weight ratio = 14/86), and the properties of the resulting thermoplastic resin composition were measured. The results are shown in Table 3.

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Table 3

| Example No. | Composition (Weight %) | | | Properties | | | | | | | |
|-------------|------------------------|----------|--------|------------|-------|--|--|---------------------------------|---|-------------------------|------------------------|
| | PP (1) | SEBS (2) | PC (3) | EPR (4) | Other | Flexural Modulus X 10 ⁴ Pa (kgf/cm ²) | Izod Impact Strength X 10 ⁴ Pa (kgf/cm) | Tensile Elongation at Break (%) | Dynamic Melt Viscosity Pa·s (x10 ⁻³ poise) | Surface Peel Resistance | Solvent Resistance (5) |
| 9 | 70 | 5 | 20 | 5 | - | 107873 (1000) | 147.1 (8.0) | 110 | 280 (2.8) | 100 | 0.20 |
| 10 | 50 | 20 | 20 | 10 | - | 82376 (8400) | 274.6 (8.0) | 98 | 300 (3.0) | 100 | 0.23 |
| 11 | 40 | 20 | 30 | 10 | - | 87279 (8900) | 398.1 (8.4) | 108 | 320 (3.2) | 100 | 0.28 |
| 12 | 30 | 20 | 40 | 10 | - | 96105 (9800) | 512.9 (10.6) | 140 | 330 (3.3) | 100 | 0.42 |
| 13 | 20 | 20 | 50 | 10 | - | 94065 (10000) | 582.5 (18.4) | 142 | 350 (3.5) | 100 | 0.45 |
| 14 | 20 | 5 | 70 | 5 | - | 131409 (13400) | 824.7 (84.3) | 136 | 400 (4.0) | 100 | 0.68 |
| 15 | 20 | 30 | 30 | 20 | - | 60801 (6200) | 610.9 (62.3) | 116 | 380 (3.8) | 100 | 0.36 |
| 16 | 40 | 20 | 30 | - | 10(6) | 90221 (9200) | 443.3 (45.2) | 137 | 320 (3.2) | 100 | 0.26 |
| 17 | 40(7) | 20 | 30 | 10 | - | 80414 (8200) | 444.3 (45.3) | 114 | 310 (3.1) | 100 | 0.28 |
| 18 | 40 | 20(8) | 30 | 10 | - | 81395 (8300) | 414.8 (42.3) | 126 | 300 (3.0) | 100 | 0.29 |

- Note: (1) Polypropylene
 (2) Styrene-ethylene-butylene-styrene block copolymer
 (3) Polycarbonate
 (4) Ethylene-propylene rubber
 (5) Weight change by methanol immersion (weight %)
 (6) Ethylene-butene-1 copolymer (Tafmer X 4085 manufactured by Mitsui Petrochemical Industries, Ltd.)
 (7) Propylene block copolymer (BJ 309 manufactured by Tonen Sekiyu Kagaku K.K., MFR = 9g/10 min)
 (8) Kraton G-1657 (manufactured by Shell Kagaku K.K., styrene/rubber weight ratio = 14/86)

55 Comparative Examples 9, 10

Thermoplastic resin compositions were prepared in the same manner as in Example 9 except for using a two-component system consisting of the crystalline polypropylene and the polycarbonate, and their

properties were measured. The results are shown in Table 4.

Comparative Example 11

5 Crystalline polypropylene (MFR = 9.0 g/10 min), a polycarbonate resin (Panlite™ L 1225 manufactured by Teijin Chemicals, Ltd.) and an ethylene-propylene rubber (Tafmer P 0180 manufactured by Mitsui Petrochemical Industries, Ltd.) were mixed in the proportions shown in Table 4 at room temperature in a Henschel mixer. The resulting mixtures was then kneaded at 250 °C in a double-screw extruder to provide composition pellets.

10 The properties of the resulting thermoplastic resin composition was measured in the same manner as in Example 9. The results are shown in Table 4.

Comparative Example 12

15 Comparative Example 11 was repeated except for replacing the ethylene-propylene rubber by a styrene-ethylene-butylene-styrene block copolymer (Kraton G™ 1650 manufactured by Shell Kagaku K.K.), and the properties of the resulting thermoplastic resin composition were measured. The results are shown in Table 4.

Comparative Example 13

20 Example 11 was repeated except for replacing the ethylene-propylene rubber by an ethylene-vinyl acetate copolymer (NUC DQ DJ 3269 manufactured by Nippon Unicar Co., Ltd.), and the properties of the resulting thermoplastic resin composition were measured. The results are shown in Table 4.

Comparative Example 14

25 Example 11 was repeated except for replacing the ethylene-propylene rubber by an ethylene-ethyl acrylate copolymer (NUC 6570 manufactured by Nippon Unicar Co., Ltd.), and the properties of the resulting thermoplastic resin composition were measured. The results are shown in Table 4.

Comparative Example 15

30 In the case of 100 weight % polycarbonate, the resin's properties were similarly measured. The results are shown in Table 4.

Comparative Example 16

35 A thermoplastic resin composition was prepared in the same manner as in Example 9 except for increasing the total amount of the styrene-ethylene-butylene-styrene block copolymer and the ethylene-propylene rubber to 60 weight % (150 parts by weight per 100 parts by weight of the polypropylene + the polycarbonate), and its properties were measured. The results are shown in Table 4.

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Table 4

| Comparative Example No. | Composition | | | | Flexural Modulus X 10 ⁴ Pa ₂ (kgf/cm ²) | Izod Impact Strength X 10 ⁴ Pa (kgf/cm ²) at 23°C at -30°C | Properties | | | Solvent Resistance (5) | |
|-------------------------|-------------|----------|--------|---------|---|---|--------------|-------------------------------|---|------------------------|-------------------------|
| | PP (1) | SEBS (2) | PC (3) | EPR (4) | | | Other (4) | Tensile Strength at Break (%) | Dynamic Melt Viscosity (x10 ³ poise) | | Surface Peel Resistance |
| 9 | 50 | - | 50 | - | 155921 (15900) | 34.2 (3.9) | 40.2 (4.1) | 6 | 310 (9.1) | 0 | 0.48 |
| 10 | 70 | - | 30 | - | 151022 (15400) | 30.4 (3.1) | 35.3 (3.6) | 11 | 310 (9.1) | 0 | 0.27 |
| 11 | 50 | - | 30 | 20 | 90221 (9200) | 51.9 (5.3) | 31.7 (3.2) | 21 | 320 (3.2) | 0 | 0.30 |
| 12 | 50 | 20 | 30 | - | 94105 (9800) | 78.4 (8.0) | 33.3 (3.4) | 131 | 320 (3.2) | 85 | 0.37 |
| 13 | 40 | 20 | 30 | - | 70607 (7200) | 147.1 (15.0) | 50.0 (5.1) | 15 | 350 (3.5) | 45 | 0.30 |
| 14 | 40 | 20 | 30 | - | 71588 (7300) | 120.6 (12.3) | 46.1 (4.7) | 18 | 360 (3.5) | 56 | 0.30 |
| 15 | - | - | 100 | - | 191230 (19500) | 612.9 (62.5) | 122.6 (12.5) | 102 | 1800 (1.8) | 100 | 1.60 |
| 16 | 20 | 40 | 20 | 20 | 23536 (2400) | 561.8 (58.0) | 240.3 (29.6) | 52 | 620 (5.2) | 100 | 0.35 |

Note: (1) Polypropylene

(2) Styrene-ethylene-butylene-styrene block copolymer

(3) Polycarbonate

(4) Ethylene-propylene rubber

(5) Weight change by methanol immersion (weight %)

(6) Ethylene-vinyl acetate copolymer (NUC PQ DJ 3269 manufactured by Nippon Unicar Co., Ltd.)

(7) Ethylene-ethyl acrylate copolymer (NUC 6570 manufactured by Nippon Unicar Co., Ltd.)

It is clear from Tables 3 and 4 that the thermoplastic resin compositions of the present invention have much better flexural modulus, impact strength, tensile elongation, moldability (shown by dynamic melt viscosity), surface peel resistance and solvent resistance than those outside the scope of the present invention (Comparative Examples).

As described above in detail, since the thermoplastic resin composition of the the present invention contains the above-described additional components, the compatibility between the polycarbonate and the polyolefin is improved. Accordingly, it has well-balanced properties such as mechanical strength, impact strength, thermal deformation resistance, surface peel resistance, moldability, chemical resistance, etc. The thermoplastic resin composition of the present invention having such properties are highly suitable as engineering plastic materials for parts of automobiles, and electric appliances.

Claims

- 10 1. A thermoplastic resin composition comprising:
 - (a) 95-5 weight % of crystalline polyolefin having a crystallinity of 20% or more
 - (b) 5-95 weight % of polycarbonate, and
 - (c) 5-100 parts by weight, per 100 parts by weight of said (a) + said (b), of a styrene-ethylene-propylene block copolymer having a weight average molecular weight of 10,000 - 1,000,000 and a weight ratio of styrene to ethylene-propylene of 15/85 - 70/30.
- 15 2. A thermoplastic resin composition comprising:
 - (a) 95-5 weight % of crystalline polyolefin having a crystallinity of 20% or more
 - (b) 5-95 weight % polycarbonate
 - 20 (c) a styrene-ethylene-butylene-styrene block copolymer having a weight average molecular weight of 10,000 - 1,000,000 and a weight ratio of styrene to ethylene-butylene of 10/90 - 70/30 and
 - (d) a low-crystallinity ethylene- α -olefin copolymer, having a weight average molecular weight of 30,000 - 1,000,000 and a crystallinity of less than 20% and a weight ratio of ethylene to α -olefin of 20/80 - 85/15 said (c) + said (d) being 5-100 parts by weight per 100 parts by weight of said (a) +
 - 25 (b), and a weight ratio of said (c) to said (d) being 30/70 - 95/5.
3. A thermoplastic resin composition as claimed in Claim 1 or Claim 2 wherein the weight average molecular weight of the polyolefin is 10,000 - 1,000,000.
- 30 4. A thermoplastic resin composition as claimed in Claim 1, 2 or 3 wherein the melt flow rate (MFR) of the polyolefin is 500-0.01 g/10 min. at 230 °C.

Patentansprüche

- 35 1. Thermoplastische Kunststoff-Zusammensetzung, bestehend aus:
 - (a) 95-5 Gew.-% kristallines Polyolefin mit einer Kristallinität von 20 % oder mehr,
 - (b) 5-95 Gew.-% Polycarbonat und
 - (c) 5-100 Gewichtsteile je 100 Gewichtsteile von (a) und (b) eines Styrol-Ethylen-Propylen-Blockcopolymer mit einem Gewichtsmittelwert des Molekulargewichts von 10.000 - 1.000.000 und einem Gewichtsverhältnis von Styrol zu Ethylen-Propylen von 15/85 - 70/30.
- 40 2. Thermoplastische Kunststoff-Zusammensetzung, bestehend aus:
 - (a) 95-5 Gew.-% kristallines Polyolefin mit einer Kristallinität von 20 % oder mehr,
 - (b) 5-95 Gew.-% Polycarbonat,
 - 45 (c) einem Styrol-Ethylen-Butylen-Styrol-Blockcopolymer mit einem Gewichtsmittelwert des Molekulargewichts von 10.000 - 1.000.000 und einem Gewichtsverhältnis von Styrol zu Ethylen-Butylen von 10/90 - 70/30 und
 - (d) einem Ethylen- α -Olefin-Copolymer einer niedrigen Kristallinität mit einem Gewichtsmittelwert des Molekulargewichts von 30.000 - 1.000.000 und einer Kristallinität von weniger als 20 % und einem Gewichtsverhältnis von Ethylen zu α -Olefin von 20/80 - 85/15, wobei (c) und (d) 5-100 Gewichtsteile je 100 Gewichtsteile von (a) und (b) sind und ein Gewichtsverhältnis von (c) zu (d) 30/70 - 95/5 beträgt.
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3. Thermoplastische Kunststoff-Zusammensetzung nach Anspruch 1 oder Anspruch 2, bei welcher der Gewichtsmittelwert des Molekulargewichts von Polyolefin 10.000 - 1.000.000 ist.
- 55 4. Thermoplastische Kunststoff-Zusammensetzung nach Anspruch 1, 2 oder 3, bei welcher die Schmelzflußrate (MFR) des Polyolefins 500-0.01 g/10 min. bei 230 °C ist.

Revendications

1. Composition de résine thermoplastique comprenant :
- 5 (a) 95 à 5 % en poids de polyoléfine cristalline ayant une cristallinité de 20 % ou plus
 (b) 5 à 95 % en poids de polycarbonate, et
 (c) 5 à 100 parties en poids pour 100 parties en poids dudit (a) + dudit (b), d'un copolymère séquencé de styrène-éthylène-propylène ayant un poids moléculaire moyen de 10.000 à 1.000.000 et un rapport en poids du styrène au éthylène-propylène de 15/85 à 70/30.
- 10 2. Composition de résine thermoplastique comprenant :
- (a) 95 à 5 % en poids de polyoléfine cristalline ayant une cristallinité de 20 % ou plus
 (b) 5 à 95 % en poids de polycarbonate
 (c) un copolymère séquencé de styrène-éthylène-butylène-styrène ayant un poids moléculaire
 15 moyen de 10.000 à 1.000.000 et un rapport en poids de styrène par rapport à l'éthylène-butylène de 10/90 à 70/30 et
 (d) un copolymère d'éthylène- α -oléfine de faible cristallinité ayant un poids moléculaire moyen de 30.000 à 1.000.000 et une cristallinité inférieure à 20 % et un rapport entre de l'éthylène par rapport à l' α -oléfine de 20/80 à 85/15, ledit (c) + ledit (d) étant de 5 à 100 parties en poids pour 100 parties
 20 en poids dudit (a) + (b), et un rapport en poids dudit (c) par rapport audit (d) qui est de 30/70 à 95/5.
3. Composition de résine thermoplastique telle que revendiquée à la revendication 1 ou la revendication 2, dans laquelle le poids moléculaire moyen de la polyoléfine est de 10.000 à 1.000.000.
- 25 4. Composition de résine thermoplastique telle que revendiquée à la revendication 1, 2 ou 3 dans laquelle l'indice de fluidité à chaud (MFR) de la polyoléfine est de 500 à 0.01 g/10 min. à 230 °C.

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